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Properties of Novel CVD Graphite Fibers and Their Bromine Intercalation Compounds

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SUMMARY

A hybrid fiber with a PAN core surrounded by a vapor-grown carbon fiber (VGCF) sheath has been fabricated using a proprietary process. The density, ultimate tensile strength, Young's modulus, and resistivity of pristine and bromine intercalated fibers made by this technique having diameters varying from 5 to 50 μm were compared with the values predicted from the rule of mixtures model. For both the pristine and intercalated fibers, the density, ultimate tensile strength, and Young's modulus of the fibers were lower than predicted, but the resistivity was measured to be consistent with predictions. The lower than theoretical mechanical properties may be evidence of a low density disordered interface between the core and the sheath which would lower the density and degrade the mechanical properties, but would leave the resistivity nearly unaffected. Intercalation had little if any effect on the ultimate tensile strength and Young's modulus, but raised the density by about 11 percent, and lowered the resistivity by an order of magnitude. The diameter dependence of the resistivity showed evidence of a depletion layer of the type found in VGCF.

INTRODUCTION

The blending of carbon fiber technology and graphite intercalation science has the potential to lead to high strength, light weight electrical conductors that could replace metallic conductors in such applications as power buses, control wiring, electromagnetic interference shielding, and lightning strike protection of aircraft. The technological difficulties in bringing this about to date, however, have proved to be unyielding. Intercalation can improve the conductivity of a graphite fiber by no more than about one order of magnitude, so it has become apparent that in order to realize this goal there must be major improvements in the crystallinity, and thus conductivity, of the carbon fibers.

Various chemical vapor deposition (CVD) processes have been used to produce highly crystalline graphite fibers, commonly known as vapor-grown carbon fibers (VGCF) [1]. The resistivity of these fibers has been found to be quite low (60 - 100 $\mu\Omega$-cm) [2], and their thermal conductivity extraordinarily high (2000 W/m-K) [3]. These fibers, however, have suffered from the technological drawback of being available only in short lengths (a few cm). Additionally, they usually have very non-uniform diameters both within a single fiber and from one fiber to the next. They are often branched and grown together, and thus not conducive to formation into prepreg tapes and fabrics. While they are suitable for some chopped fiber applications, new fabrication techniques must be developed before they will see widespread use as structural materials.

One possible solution to these problems has been to develop a hybrid fiber with a PAN fiber core, and a VGCF shell [4]. It might be possible to create a continuous process by which PAN fibers could be coated with VGCF, and processed very much like conventional PAN fibers. Ideally, the resulting fiber would have mechanical properties similar to PAN, and transport properties similar to VGCF.

Deposition of a highly graphitic layer around the PAN fiber also enables the fiber to be intercalated [4]. Since the added layer is highly graphitic, intercalation lowers the resistivity by about an order of magnitude, and the resulting fiber has a resistivity comparable to many metals.

In this study we report preliminary properties of hybrid PAN-VGCF fibers which are relatively long, straight, and unbranched that were made by a proprietary process. In addition, the production process allows for convenient alteration of the fiber diameter by subtle changes in the process variables, so particular attention is focused on the variability of properties as a function of fiber diameter (ie. as a function of percent VGCF). We also report on the effects of bromine intercalation upon the mechanical properties and resistivity of these same fibers.

EXPERIMENTAL

The fibers were prepared at Applied Sciences, Inc., using a proprietary CVD process which enabled the growth of long, (tens of cm) straight fibers. By altering processing parameters fibers with diameters ranging from about 6 to about 60 μm were produced. The Amoco T-650 PAN fibers used for the core had a diameter of about 5 μm, a density of 1.789, an ultimate tensile strength (UTS) of 5.25 GPa, a Young's modulus of 290 GPa, and an initial resistivity of about 2000 $\mu\Omega$-cm. A 6 μm diameter hybrid fiber would be composed of about 30 percent VGCF, and the 60 μm diameter over 99 percent VGCF. Fibers of 7 μm diameter would be half PAN and half VGCF by volume. The fibers were heat-treated by UCAR Carbon (Parma, Ohio) to about 2900 °C.

Since fiber diameter was an important parameter in this study, they were measured using a single slit-like diffraction technique [5]. Our apparatus gave diameter results which were reproducible to within about 2 percent. Unlike conventional VGCF, most of these fibers had very little taper over the measurement length (about 1 cm). Four-point resistivity [6] and gradient column density [7] were measured using standard techniques which have been previously reported. Ultimate tensile strength (UTS) and Young's

Modulus were measured using an Instron model TTC Universal Testing Instrument with a 50 g load cell.

Bromine was intercalated into the fibers via a vapor phase reaction at room temperature. The partial pressure of bromine was about 22 kPa (165 torr). The reaction was allowed to proceed for about 50 hours, and then the fibers were allowed to degas for at least three weeks. Previous studies indicate that this should result in a stable residual intercalation compound in VGCF [8].

Formation of a bromine intercalation compound was confirmed both by x-ray diffraction and by detection of the characteristic two-dimensional melting endotherm near 100 °C using differential scanning calorimetry [9].

RESULTS AND DISCUSSION

Rule of Mixtures

The rule of mixtures assumes that there is no interaction between the two components of a composite, in this case, the hybrid fiber. Thus, the composite property is an average weighted by the volume of the components, or in this case:

$$p_{hybrid} = p_{PAN}v_{PAN} + p_{VGCF}v_{VGCF}$$

where p_{hybrid}, p_{PAN}, and p_{VGCF} are the property values (density, UTS, Young's modulus, or electrical conductivity) of the hybrid fiber, the PAN fiber, and the VGCF fiber respectively, and v_{PAN} and v_{VGCF} are the volume fractions of PAN and VGCF respectively (it is assumed that the properties of the sheath are similar to that of VGCF). Since the absolute volume of the PAN component is constant, the relative volume fraction drops as the hybrid fiber diameter increases. Thus the property starts from the PAN value and approaches asymptotically the VGCF value as the diameter increases.

Density

The density of the PAN fiber is about 1.8 g/cm^3 and the density of well graphitized VGCF is about 2.15 g/cm^3 (though there is a wide variation) [10]. The rule of mixtures density for the pristine hybrid fibers is plotted in figure 1, along with the measured data. Rather than predicting the density, the rule of mixtures seems to place an upper bound on the density. Scanning electron microscopy suggests that the high temperature heat treatment may severely damage the core of PAN fiber. Perhaps there are large disordered or even void regions at the PAN-VGCF interface. This notion is supported by the data of fibers with large diameters (above 35 μm) which lie closed to the rule of mixtures line.

Bromine intercalation would be expected to increase the density of the fibers. The only modification in the rule of mixtures model is to use the density of intercalated VGCF in the place of the pristine. Previous studies suggest a density of about 2.35 g/cm^3 for bromine intercalated VGCF. The pristine PAN density was used in the rule of mixtures calculation because under the intercalation conditions used for the hybrid fibers, the PAN fiber does not intercalate bromine [10].

The upper line in figure 1 is the rule of mixtures density for bromine intercalated hybrid fibers. As in the case of the pristine fibers, it represents a limiting value rather than a predictive one. Once again, when the diameter exceeds about 35 μm, densities fall closer to the line. Intercalation does not seem to change the functional form of the diameter dependence, it merely shifts the curve upward by about 9 percent. It is interesting to note that this is only half of the weight uptake of the residual bromine intercalation compound in P-100 fibers.

Mechanical Properties

The determination of the UTS of the fibers met with only limited success because the fiber gauge lengths were short (10 - 13 mm). There was a wide variation in the UTS values, from about 0.1 to 3 GPa. The UTS of vapor-grown fibers has been found to be limited by gross defects such as branching, inclusions and nodules and, for fibers without such detected flaws the UTS has been reported to be about 1.3 GPa [11]. Figure 2 shows the variation of UTS with diameter, and the expected relation from the rule of mixtures, assuming a 1.0 GPa UTS for the VGCF sheath. A UTS value of 0.45 GPa gives a better fit to the data, but the scatter is still so large as to prohibit definitive conclusions.

The UTS values for the bromine intercalated fibers are also shown in figure 2. Once again there is a large variation, but in general the values tend to fall in the same area as the pristine. The UTS of intercalated pitch-based fibers has been shown to be decreased only by that amount expected by the expansion of the fiber due to the intercalation process [12]. The data also show no indication of catastrophic loss of strength.

The Young's modulus of the fibers varied from about 20 to 220 GPa, and showed a strong diameter dependence. Figure 3 shows these data along with the rule of mixture predictions for 150 GPa modulus, as has been reported for VGCF [13]. This value predicts a much higher value for the modulus than was observed. A sheath modulus value of about 25 GPa is a more successful predictor, but the fit still is not good.

The effect of bromine intercalation upon the Young's modulus was found to be small. Although there seems to be some degradation, again the scatter is too large to make a confident judgement.

Electrical Resistivity

The rule of mixtures for the resistivity of a hybrid fiber is equivalent to a parallel resistor model. In this model it is assumed that no current flows between the core and the sheath, so lattice disruptions and voids along the interface should not disrupt the resistivity as long as the current is injected uniformly into the end of the fiber. In practice, however, the current is both injected and the voltage sensed from the outer sheath. It would not be surprising then if the rule of mixtures predicts well for thick fibers, but not as well for fibers with a thin sheath.

Figure 3 indicates that this is indeed the case. The resistivity of the PAN fiber was assumed to be 2000 $\mu\Omega$-cm, and that of the sheath was assumed to be 70 $\mu\Omega$-cm. For fiber diameters in excess of about 15 μm the rule of mixtures predicts the resistivity quite well, but not so for thinner fibers.

The effect of bromine intercalation is to lower the resistivity by about an order of magnitude (fig. 4). In the rule of mixtures model, the resistivity of the intercalated VGCF was assumed to be 7 $\mu\Omega$-cm. However, unlike the pristine fibers there seems to be three diameter regimes with different amounts of agreement with the rule of mixtures prediction. For thin fibers (less than 10 μm) the model is off by about two orders of magnitude. For the region between 10 and 30 μm the model is about a factor of 2 lower than the data. The resistivity is well predicted for fibers thicker than about 30 μm. Interestingly, there is also a group of fibers in the 10 to 30 μm range with very low resistivities (about 2 $\mu\Omega$-cm).

It has been shown in a number of studies that there is a depletion zone around the outer boundary of the residual bromine intercalation compound [14]. If we assume the 3 μm depletion zone proposed by Gaier for VGCF, the rule of mixtures, using the pristine VGCF resistivity for the depletion zone, predicts the diameter dependence of the resistivity shown in figure 4. This is a much better fit for fibers with diameters of 10 μm and larger.

There are still the group of fibers with unaccounted for, and unexpectedly low, resistivities. The density of these fibers might be expected to be higher than those of the other fibers due either to more crystalline order in the fiber, or to a higher concentration of intercalate. However, if the densities of the seven fibers with resistivities lower than 5 $\mu\Omega$-cm are examined, it is found that they range from 2.02 to 2.31 g/cm^3, typical of the intercalated fibers (see fig 1.). It is not obvious why the resistivities of these fibers are so low.

CONCLUSIONS

A hybrid fiber with a T-650 PAN core surrounded by a VGCF sheath has been fabricated using a proprietary process. The density, ultimate tensile strength, Young's modulus, and resistivity of fibers of diameters varying from 5 to 50 μm were compared with the values predicted from the rule of mixtures model. For both the pristine and intercalated fibers, the density, ultimate tensile strength, and Young's modulus of the fibers were lower than predicted, but the resistivity was predicted correctly. This can be explained by a low density disordered interface between the core and the sheath. This would lower the density and degrade the mechanical properties, but since virtually all of the electrical current would flow through the sheath, it would leave the resistivity virtually unaffected.

Bromine intercalation was found to have little if any effect on the ultimate tensile strength and Young's modulus, but raised the density by about 11 percent, and lowered the resistivity by an order of magnitude. The diameter dependence of the resistivity was better predicted by a three component rule of mixtures model assuming a 3 μm bromine depletion layer of the type found in VGCF.

Further improvements in fiber production and intercalation technology are expected to lead to applications where high conductivity and strength and low density are required.

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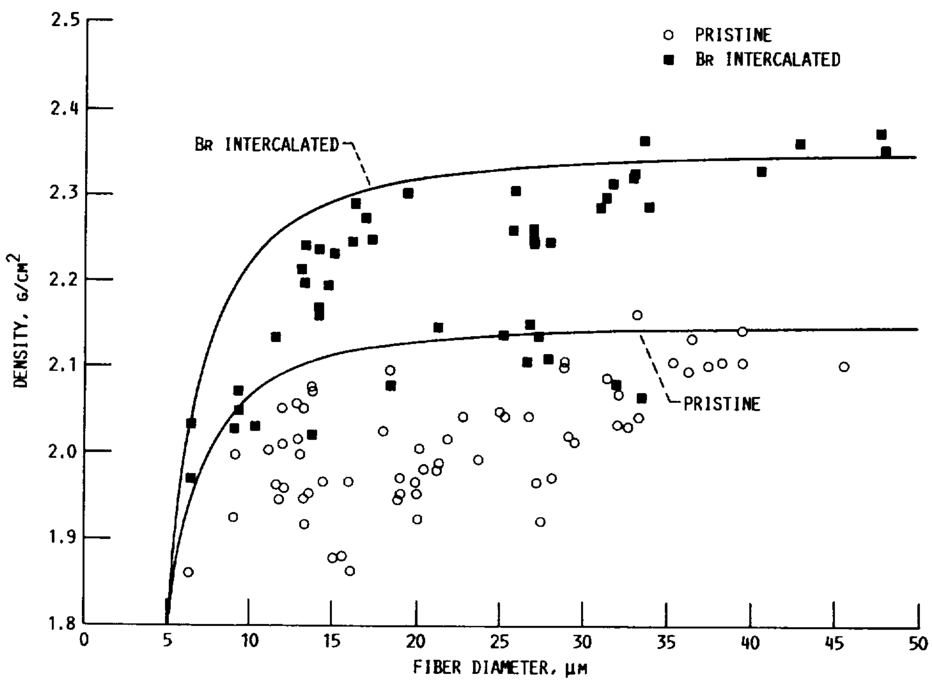

FIGURE 1. - THE DENSITY OF PRISTINE AND BROMINE INTERCALATED HYBRID FIBERS COMPARED TO THAT PREDICTED BY THE RULE OF MIXTURES.

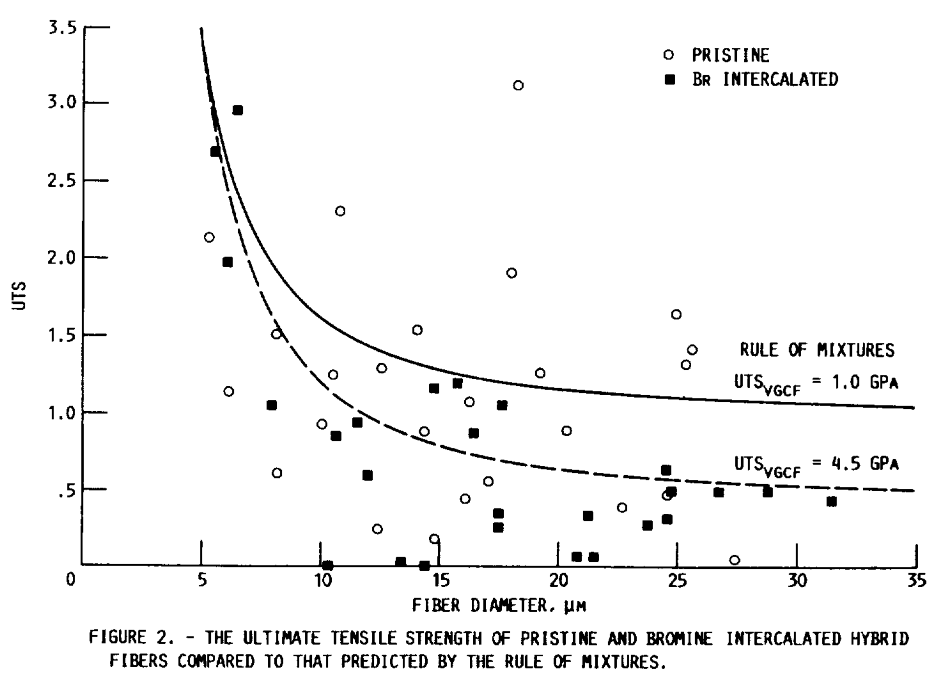

FIGURE 2. - THE ULTIMATE TENSILE STRENGTH OF PRISTINE AND BROMINE INTERCALATED HYBRID FIBERS COMPARED TO THAT PREDICTED BY THE RULE OF MIXTURES.

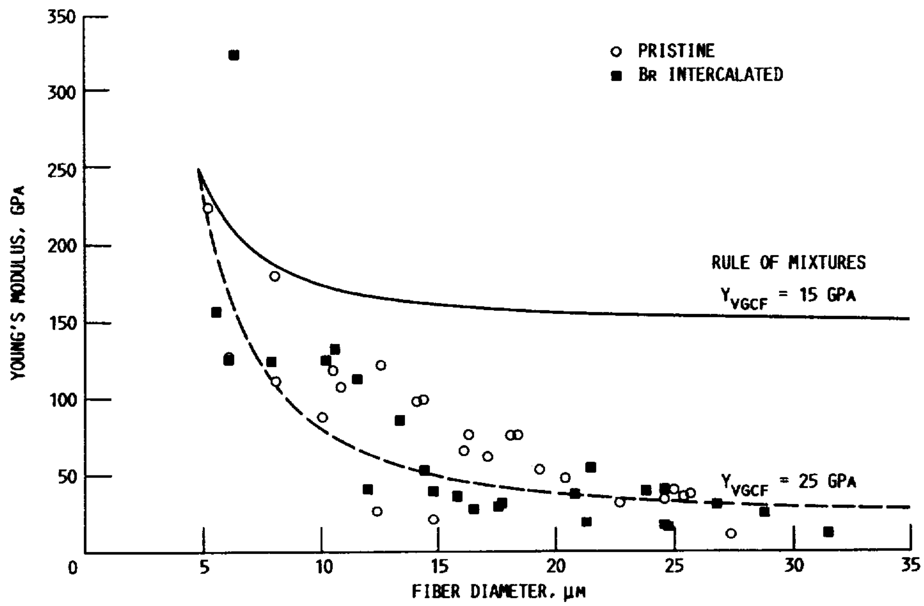

FIGURE 3. - THE YOUNG'S MODULUS OF PRISTINE AND BROMINE INTERCALATED HYBRID FIBERS COMPARED TO THAT PREDICTED BY THE RULE OF MIXTURES.

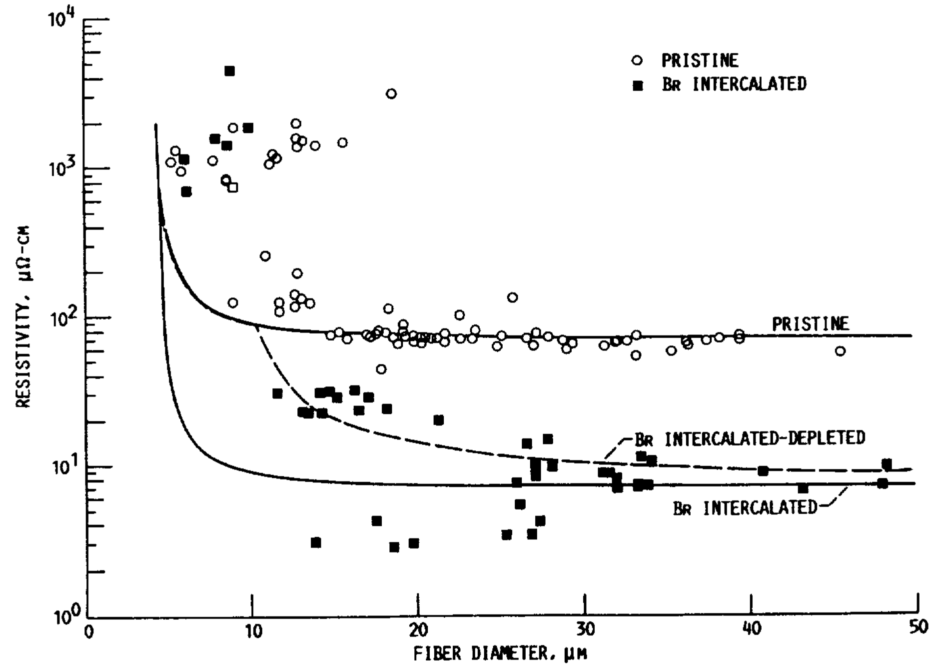

FIGURE 4. - THE RESISTIVITY OF PRISTINE AND BROMINE INTERCALATED HYBRID FIBERS COMPARED TO THAT PREDICTED BY THE RULE OF MIXTURES. THE DASHED LINE ASSUMES A 3 μm DEPLETION LAYER.

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13. ABSTRACT *(Maximum 200 words)*

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